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Copper(II) Nitrate-(\pm)-1-Phenylethylamine

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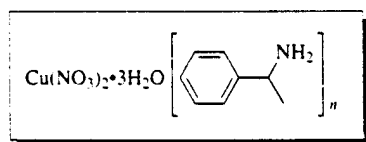
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Copper(II) Nitrate-(±)-1-Phenylethylamine¹



$(\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O})$		
[10031-43-3]	$\text{H}_6\text{CuN}_2\text{O}_9$	(MW 241.60)
$((\pm)\text{-PhCH}(\text{Me})\text{NH}_2)$		
[618-36-0]	$\text{C}_8\text{H}_{11}\text{N}$	(MW 121.18)

(reagent for the oxidative coupling of phenols²)

Physical Data: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$: mp 114 °C. (±)-1-Phenylethylamine: bp 185 °C/756 mmHg; d 0.95 g cm⁻³. The exact structure of the copper(II) complex is unknown; the number of phenylethylamine ligands is preferentially 4 ($n = 4$).

Form Supplied in: the reagent is prepared in situ; both compounds are commercially available. (±)-1-Phenylethylamine is a colorless oil; copper(II) nitrate trihydrate is a blue crystalline deliquescent material.

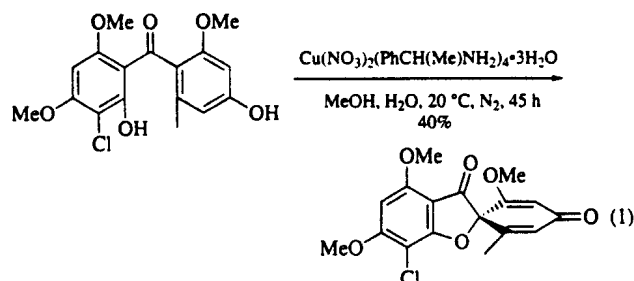
Analysis of Reagent Purity: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$: > 99%. (±)-1-Phenylethylamine: ¹H NMR (CDCl_3 , 200 MHz) δ 1.37 (d, $J = 6.4$ Hz, 3H), 4.07 (q, $J = 6.7$ Hz, 1H), 7.19-7.33 (m, 5H); ¹³C NMR (CDCl_3 , 50.29 MHz) δ 25.2 (q), 50.8 (d), 125.2 (d), 126.3 (d), 127.9 (d), 147.3 (s).

Preparative Methods: prepared in situ by complexation of copper(II) nitrate with 4 equiv of (±)-1-phenylethylamine in methanol under inert atmosphere.^{1,2}

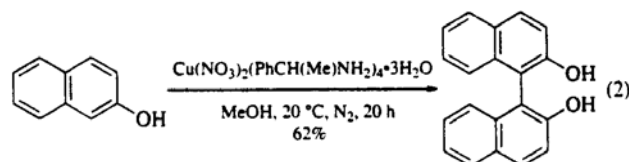
Handling, Storage, and Precautions: (±)-1-phenylethylamine is stable when stored in a sealed container under nitrogen.

General Considerations. The copper(II) nitrate-(±)-1-phenylethylamine reagent (**1**) is a typical example of a number of copper(II) amine oxidizing agents.¹⁻³ Reagent (**1**) can effect the oxidative coupling of phenols under anaerobic conditions. Both C-C and C-O coupled products can be obtained. Characteristic examples are given.

Synthesis of Dehydrogriseofulvin. Reaction of (**1**) with bis-phenols leads to intramolecular C-O coupled products (eq 1).¹



Synthesis of 1,1'-binaphthalene-2,2'-diols. The oxidative dimerization of 2-naphthols with (**1**) provides 1,1'-binaphthols (eq 2).²



Unsymmetrical 1,1'-binaphthalene-2,2'-diols are formed in 80-97% yield by oxidative cross-coupling of differently substituted 2-naphthols mediated by related Cu^{II}-primary amine complexes.^{3b} (S)-(-)-1,1'-Binaphthalene-2,2'-diol and (S)-(-)-10,10'-dihydroxy-9,9'-biphenanthryl have been prepared with optical purities up to 98% by a similar oxidative coupling using chiral nonracemic primary amines.^{1,3a,3d}

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